

PATENT

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THERMALLY CONDUCTIVE FLUOROCARBON POLYMER COMPOSITE

FIELD OF THE INVENTION

5 The present invention relates to thermally conductive polymer composite materials, conductive members and surfaces containing such materials, to heat exchange equipment containing such members and surfaces, and to methods of making each of these.

10 BACKGROUND OF THE INVENTION

Numerous applications require the transfer of heat across or through a thickness of solid material. For example, home heating systems typically conduct heat from hot air or water through the wall of the conduit or duct, which contains the hot fluid. Other applications, which require such a transfer of heat, include
15 automotive heater cores, radiators, evaporators, condensers, charge air coolers, and transmission/engine oil coolers. Such devices, and many others that operate on the same principle, are typically referred to as heat exchange devices. Heat exchange devices play a critical role in many industrial applications, especially in the chemical, petroleum and power industries.

20 The material, which forms the wall through which heat flows in such devices most desirably, has a high degree of thermal conductivity. Thermally conductive metals, such as aluminum, copper and frequently more exotic metals and alloys have heretofore been frequently used for their desirable combination of strength and good thermal conductivity. However, such materials do not always
25 possess the best overall combinations of properties for particular applications. For example, in many applications in the chemical industry the heat exchange surface must be in contact with highly corrosive chemicals. Metals, which are adequate in such environments, are often detrimentally expensive. The requirement of good thermal conductivity and excellent resistance to corrosion is also present in
30 certain battery applications, as disclosed for example in U.S. Patent No. 5,786,107, which is incorporated herein by reference.

5 In other applications, the metallic products, which have heretofore been used, are not easily formed into the shape required by certain heat exchange devices. For example, many heat exchange devices require the use of tubes with fins or similar projections in order to increase the heat transfer surface. Forming such an arrangement from metals is frequently difficult, time consuming and expensive. Furthermore, there has been a trend in the industry to form such devices with very thin fins, and this trend has caused a variety of problems for heat exchange equipment in which the heat transfer surfaces are formed from metallic materials, as noted in U.S. Patent No. 6,329,075.

10 Advances in the electronics industry have also created a need for improved heat conducting materials. As electronic components, especially computers and similar devices, which rely on microprocessors, operate at faster and faster speeds and become smaller and smaller, the problem of managing the heat generated by such devices becomes critical. For instance, heat build-up in electronic products leads to reduced reliability ("mean-time-to-failure"), slower performance, and reduced power-handling capabilities. In addition, continued interest in increasing the number of electronic components on, and reducing the size of, semiconductor chips, notwithstanding the desire generally to reduce power consumption thereof, also contributes to the importance of thermal management. Also, chip-on-board technology, where semiconductor chips are mounted directly to printed circuit boards, creates further demands on thermal management because of the more efficient use of surface area thereon.

20 Thermal management techniques include generally convection and/or conduction mechanisms, where heat may be removed from electronic devices (such as operating silicon integrated circuits) by air (e.g., free flowing or forced) convection around the device, fluid (e.g., water or other fluid) convection through radiators, evaporators, reactors and the like, or conduction through the solid parts of the heat exchange equipment which are in contact with the fluids and through which the heat must flow. A combination of such techniques is often used to maintain temperatures within design criteria.

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Heat conduction, which is the more important phenomenon for the present invention, involves heat flow per unit area over a length, which is proportional to the temperature gradient across that length. Thus, heat conduction (or thermal conductivity) is a steady-state property measuring the ability of a certain material to transfer heat there through.

The present inventors have discovered a highly desirable and advantageous polymer-based material which is especially well adapted for use as or in connection with heat transfer equipment, which has a high degree of thermal conductivity, which is readily formable into a wide variety of shapes, which has excellent corrosion resistance, and which is cost effective relative to certain heretofore used metal-based material.

SUMMARY OF THE INVENTION

The present inventors have discovered that many of the above noted difficulties are overcome by a polymer composite comprising a major proportion of fluorocarbon polymer and a minor proportion of boron nitride. As used herein the terms "boron nitride" and "B(N)" mean and identify all phases and compounds consisting essentially of boron and nitrogen. The notation "B(N)" as used herein thus indicates that some or all of nitrogen may be bound (covalently and/or ionically) to the boron, such as in BN, but is not limited to this compound. Thus, the notation "B(N)" also covers the stoichiometry BN₂, BN₃ and other effective and possible stoichiometries and/or combinations of boron and nitrogen.

DETAILED DESCRIPTION

The polymer composite of the present invention comprises a major proportion by weight of polymer resin, preferably resin comprising and even more preferably consisting essentially of fluorocarbon polymer, and from about 2 % to about 40 % by weight of B(N), more preferably from about 2 % to about 20 % by weight of B(N) and even more preferably from about 5 % to about 15 % of BN. Applicant believes that a critical range exists in the amount of B(N) used in the thermally conductive polymer composite of the present inventions. This

criticality is based on the need for the composite to at once have a difficult to achieve combination of properties. More particularly, the amount of the B(N) should be effective to substantially improve the thermal conductivity of the resin, particularly in embodiments involving fluorocarbon polymer, which would otherwise be a very poor thermal conductor. At the same time, the amount of B(N), and in certain embodiments the type and nature of the B(N), should not have a deleterious effect on the mechanical strength and stability of the composite or on the ready formability of the composite. For example when the preferred fluorocarbon polymer comprises PTFE, the preferred ranges specified herein provide ready extrudability by paste extrusion while at the same time achieving the desirable thermal and mechanical properties described above. Similarly for melt extrudable fluorocarbon polymers, such as FEP and PFA, the preferred ranges specified herein provide adequate melt strength while at the same time achieving the desirable thermal and mechanical properties in the finished product. In addition and/or as an alternative to fluorocarbon polymer, the polymer of the present invention may comprise polyolefin(s), such as polyethylene (preferably high-density polyethylene) and polypropylene.

As the term is used herein, fluorocarbon polymer refers to and is intended to include not only a single fluorocarbon polymer entity but also a mixture of any two or more fluorocarbon polymer entities. As is well known, fluorocarbon polymers are a class of paraffinic polymers, which have some, or all of the hydrogen replaced by fluorine. It is contemplated that the present composites can be formed from any one of these polymeric components. The fluorocarbon polymer component of the present composite is preferably selected from group consisting of polytetrafluoroethylene (PTFE), fluorinated ethylene propylene copolymer (FEP), perfluoroalkoxy (PFA) resin, polychlorotrifluoroethylene (PCTFE), ethylenetrifluoroethylene copolymer (ECTFE), ethylenetetrafluoroethylene copolymer (ETFE), polyvinylidene fluoride (PVDF), polyvinyl fluoride (PVF), copolymers and terpolymers including any one or more of these, and mixtures of two or more of these. While it is contemplated that all of the above fluorocarbon polymers, including homopolymers, copolymers, block

and graft copolymers of any of the above, may be used, PTFE, PFA and FEP are preferred. Furthermore, those skilled in the art will appreciate that the term "PTFE" encompasses not only pure PTFE homopolymers but also copolymers comprising greater than about 99wt%, of PTFE moieties.

5 It is contemplated that numerous types and varieties of B(N) may be used effectively in accordance with the present invention, and all such types and varieties are within the scope hereof. In certain preferred embodiments, the boron nitride used in the compositions of the present invention is in the form of a powder comprised of particles having a hexagonal crystal structure and large,
10 graphite like platelets. Such a powder is available from G. E. Advanced Ceramics of Cleveland OH under the trade designation "Boron Nitride Powder - Grade AC - 6004." In certain embodiments, the B(N) of the present invention is in the form of a powder having a hexagonal crystal structure and a mean crystal size greater than about 10 micron and a mean particle size of from about 9 to about 12
15 microns. The preferred powders are also preferably 99.9% 325 mesh, and also preferably have a surface area of about 2 square meters per gram, a tap density of about 0.55 grams/cc, and an oxygen content of about 0.3%. The preferred powders also have a particle size distribution wherein at least about 50%, and even more preferably at least about 60% of the particles have a size of from about
20 5 to about 15 microns. It is also preferred in certain embodiments that the B(N) powders have a particle size distribution wherein at least about 65%, and even more preferably at least about 70% of the particles have a size of from about 5 to about 20 microns. In certain highly preferred embodiments, the B(N) comprises, and preferably consist essentially of, powders having a particle size distribution
25 as indicated in Table I below, it being noted that the values indicated below are

deemed to all be preceded by the word "about" :

PARTICLE SIZE RANGE (MICRONS)	PERCENTAGE RANGE
1 - 1.7	0 - 1
1.7 - 2.6	1 - 2
2.6 - 3.7	3 - 5
3.7 - 5.3	5 - 9
5.3 - 7.5	15 - 20
7.5 - 10.5	20 - 25
10.5 - 14.9	20 - 25
14.9 - 21.1	10 - 15
21.1 - 29.8	2 - 5
29.8 - 42.2	0 - 2

5 According to preferred aspects of the present invention which utilize fluorocarbon polymer resins that are paste extrudable, such as PTFE, such resins are generally in the form of extrusion grade powders, fine powders, and the like. For embodiments in which the polymeric component is PTFE, it is preferred that the PTFE powders are dispersion grade and not granular. Techniques for the production of fine PTFE powders are well known, and the use of polymers produced by any of these techniques is well within the scope of this invention. For
10 example, fine PTFE powder may be produced by coagulating colloidal PTFE particles as disclosed in U.S. Pat. No. 4,451,616, which is incorporated herein by reference.

For resins that are melt extrudable, it is contemplated that a wide variety of conditions and process parameters can be used within the scope of the present
15 invention. In certain embodiments, it is preferred that extrusion temperature ranges from about 500°F to about 800°F, more preferably about 550°F -700°F, with the screw revolutions per minute (RPM) ranging from about 1 to about 100 RPM, more preferably 5-50 RPM.

20 Although it is contemplated that the amount of fluorocarbon polymer used in the present composite can vary widely within the scope of the present invention, it is generally preferred that the composite comprise at least about 60%

by weight of fluorocarbon polymer, more preferably at least about 75% by weight of fluorocarbon polymer, and even more preferably at least about 85% by weight of fluorocarbon polymer.

5 In preferred embodiments, the present composite is a formed composite, such as a film, plate, tubular member, finned tubular member and the like, having a thermal conductivity which is at least 50%, and even more preferably at least about 100% greater than the thermal conductivity of the same formed product except in the absence of the B(N). In preferred embodiments, the present invention provides formed composites having a thermal conductivity, T_c , of at least about 1.5 (W/m/K), more preferably at least to about 2 (W/m/K) and even more preferably at least to about 2.5 (W/m/K). As will be appreciated by those skilled in the art, these values compare very favorably to the value, for example, of neat FEP resin, which has a thermal conductivity of about 1.1 (W/m/K). In highly preferred embodiments, the formed composite has a thermal conductivity of at least about 3 (W/m/K).

10 The present composites may optionally include other fillers (both organic and inorganic), lubricants, pigments and other modificants as will be appreciated by those skilled in the art. The composites of the present invention can be formed by a wide variety and combination of techniques in view of the teachings contained herein, and all such methods are within the broad scope of the present invention. In preferred embodiments, however, the composite is formed by intimate mixing of the fluorocarbon polymer and the B(N) under conditions effective to achieve a substantially homogeneous mixture of thereof. One preferred method for formulating such composites comprises mixing the polymer resin, and preferably fluorocarbon polymer in the form of fine powders, with particulate B(N). Another method is co-coagulation of the resin and the B(N). Any well known mixing process that achieves homogeneous and uniform mixing may be employed; although for paste extrusion techniques mixing by tumbling in a suitable commercial blender such as a Patterson Kelly Twin Shell at 15 20 25 30 temperatures up to about 68°F for a period of about 3 minutes is generally

preferred. For melt processes, it is expected that twin-screw type mixing techniques are commonly used, but all other applicable techniques are also within the scope of the present invention.

5 The heat exchange structures of the present invention can be formed by a wide variety and combination of techniques in view of the teachings contained herein, and all such methods are within the broad scope of the present invention. In preferred embodiments, however, the particles of B(N) are blended with the fluoropolymer in amounts sufficient to attain a composite that is at once readily extrudable (most preferably by paste extrusion in the case of PTFE), has a
10 relatively high structural integrity, and has a thermal conductivity in accordance with the present invention. In general, it is preferred according to the present invention that the shaped composites of the present invention are produced by paste extrusion. In the paste extrusion process, the resin (preferably fluorocarbon polymer), the B(N) and any other modificants which may be present, are
15 integrated into a substantially homogeneous mass and then compressed into the appropriate pre-formed shape, preferably a cylindrical shape, by techniques well known in the art. An extrusion aid, such as naphtha or other volatile paraffinic hydrocarbon, may be added to the pre-formed composite, preferably in an amount of from about 15% to about 20% by weight. The pre-formed composite is then
20 shaped into the desired form by cold flow extrusion according to techniques well known in the art.

After extrusion, the extrusion aid is substantially removed from the shaped article. According to one embodiment, removal of the extrusion aid comprises heating the shaped composite for time and at a temperature sufficient to
25 effect removal of the extrusion aid, typically for about 15 seconds at about 350°F. The shaping process further preferably comprises a sintering step in which the extruded composite is heated for time and at a temperature sufficient to fuse or sinter the compressed powders into a homogeneous product, typically for about 20 seconds at about a temperature of at least about 647°F (342°C). The shaping
30 process may be, and preferably is, carried out continuously.

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While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustrations and not limitation.

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